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Final Project Report

Constitutive Behavior of Relaxor Single Crystals

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Technical Objectives

The objectives of program from July 2005 through May 2007 involved a collaboration between Beth McLaughlin (replaced by Hal Robinson in the final year) at NUWC - Newport Division, Markys Cain, and Christopher S. Lynch that has resulted in characterization of the phase transformation behavior of PMN-xPT relaxor ferroelectric single crystals that are in the rhombohedral phase when not loaded. This involves combined stress, electric field, and temperature loading of the crystals while monitoring the strain and electric displacement response (McLaughlin, Robinson); characterizing the crystal structure under load using a synchrotron (Caine); and data analysis and modeling (Lynch). This report focuses on the data analysis and modeling.

Technical Approach

Background *–from McLaughlin, Liu, Lynch, "Relaxor Ferroelectric PMN-32%PT Crystals under Stress, Electric Field, and Temperature Loading II: 33- Mode Measurements" Acta Materialia (2005)*

Relaxor ferroelectric single crystals exhibit extraordinary electromechanical properties [1]. The dielectric and piezoelectric properties of relaxor single crystals are anisotropic, nonlinear and hysteretic. Both <001> and <110> poled rhombohedral crystals $[Pb(Zn_{1/3}Nb_{2/3})O_3]_{(1-x)}$-$[PbTiO_3]_x$ (PZN-xPT, 0<x<0.1) and $[Pb(Mn_{1/3}Nb_{2/3})O_3]_{(1-x)}$-$[PbTiO_3]_x$ (PMN-xPT, 0<x<0.35) display large electromechanical coupling and piezoelectric coefficients. The physical properties of these crystals are related to their domain structures and phase states [2,3]. These crystals occur in the cubic (C), tetragonal (T), rhombohedral (R), monoclinic (M) and orthorhombic (O) phases. The phase of these crystals is a function of composition, temperature, applied stress and electric field (magnitude and direction). The high temperature phase (parent phase) has cubic symmetry. The lower temperature tetragonal (4mm), rhombohedral (3m) and orthorhombic (mm2) phases have spontaneous polarization in <001>, <111> and <110> directions, respectively. Other phases have been detected near morphotropic boundaries in the phase diagram, especially when stress or electric field is present. There are potentially three types of monoclinic phases M_A, M_B, M_C [4]. Evidence of a monoclinic phase was reported in PMN–33%PT crystals [5].

Investigations have shown that morphotropic phase boundary (MPB) compositions of the PZN-xPT and the PMN-xPT systems are in a multiphase state. Coexistence of R, M, O, or T phases affects electromechanical properties and results in complex phase behavior [6-8]. Several researchers [9-13] have observed the coexistence of rhombohedral and tetragonal domains in PZN-xPT and PMN-xPT crystals at room temperature. A study of the MPB phases of PMN-xPT by means of high-resolution synchrotron X-ray diffraction indicated that a third phase besides R and T phases is present in the composition range of 31–37%PT at temperatures around and below 25 °C [6]. Recently the extent of different phases (R, M or O, T) in PZN-xPT and the dependency of their volume fractions on the PT content were quantified [14]. It has been postulated that that coexistence of multiple phases and phase instability are critical to the extraordinary crystal properties.

The stability of the phases depends on the electrical, mechanical and thermal conditions. Changes of temperature, electric field and stress lead to polarization switching and phase transitions in these crystals and hence dramatically alter their electromechanical properties. Figure 1 is a schematic of a crystal variant representation of the average domain structure and possible phase transitions driven by electric field and stress loading in the <001> direction and in the <011> direction. An electric field induced phase transition between the rhombohedral and tetragonal (R-T) phases has been observed by many authors [15-20]. Han and Cao [21] found that application of electric field bias along <001> decreases the R-T phase transition temperature. Ren *et al.* [16] measured the R-T phase transition fields of PZN-4.5%PT and PZN-8%PT crystals as a function of temperature and found linearly decreasing field values relative to increasing temperature. After observation of temperature dependent domain structures under a polarizing microscope, Schmidt *et al.* [22] and Tu *et al.* [23] concluded that the R-T phase transition occurs as rotation of polarization through monoclinic (M) phases. Phase transitions, along with reorientation switching, induce heterogeneity in the crystals [24].

In addition, temperature and field induced phase transitions and changes of domain structures can induce cracking that leads to premature failure.

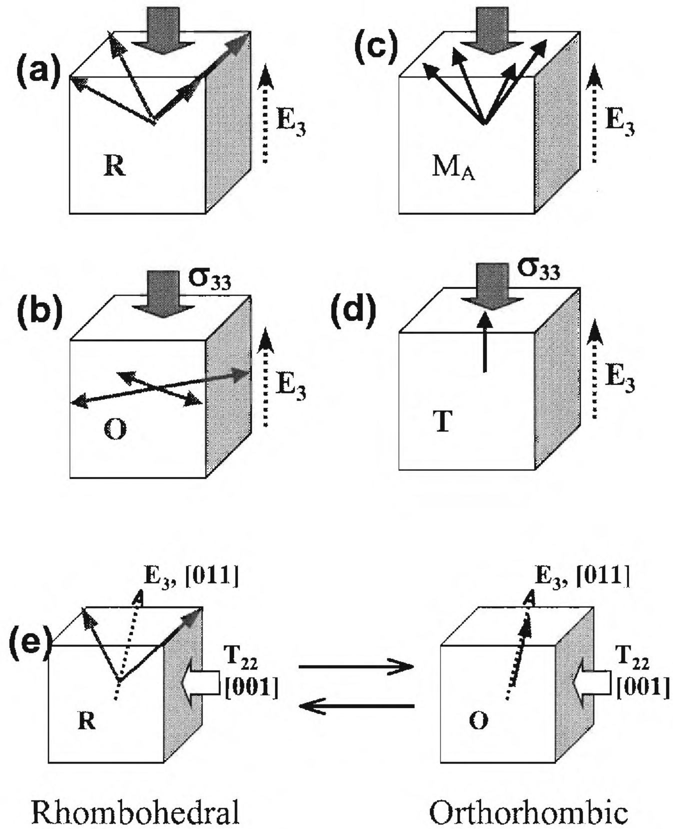

Figure 1. Possible phases and domain states of PMN-32%PT single crystals under: <001> electric field and stress loading. (a) Rhombohedral phase polarized into a four-domain state at room temperature under small stress and electric field; (b) Orthorhombic phase (depolarized) under large compressive stress and small electric field; (c) Monoclinic (M_A) phase under small stress and large electric field; (d) Tetragonal phase under small stress and larger electric field; and (e) under <011> loading.

Summary of activities

McLaughlin, Liu, and Lynch [25] published evidence of multiple phase transitions for <001> oriented PMN-32%PT single crystals under combinations of stress, electric field, and temperature loading. The results indicate that the driving force for the transformations decreases with increasing temperature. Material properties for different phases under excursions of electric field and stress are reported.

Liu and Lynch [26] published a crystal variant approach to modeling the electromechanical properties that led to the identification of engineered domain states with properties optimized for specific applications, including the large transverse piezoelectric coefficients of the <110> orientation and large 33-mode piezoelectric coefficients of the <001> orientation. Polarization switching and phase transitions under combinations of stress, electric field, and temperature loading were reported. Features of field induced phase transitions in these crystals were discussed.

In work partially supported by this grant and partially support by a prior ONR grant, Liu and Lynch [27, 28] published results pertaining to compressive stress and electric field applied to relaxor single crystals $[Pb(Zn_{1/3}Nb_{2/3})O_3]_{0.955}$-$[PbTiO_3]_{0.045}$ (PZN-4.5%PT) in a series of crystal orientations between <001> and <111>, and the corresponding strain and electric displacement response. It was found that as the angle of the orientation cut is rotated from <001> to <111>, the piezoelectric coefficient d_{33} drops and hysteresis loss increases dramatically. The piezoelectric coefficients, remnant strain and remnant electric displacement are modeled using a volume averaging of crystal variant volume fractions.

Liu and Lynch published a review of single crystal behavior in reference [29]. This review article describes the observed behavior and presents results of multiscale modeling that predicts the macroscopic behavior from the single domain single crystal behavior and evolution of crystal variants at the microscale.

Liu, McLaughlin, and Lynch [30] published an article in the Journal of Intelligent Materials Systems and Structures entitled "Thermodynamics of Stress and electric field induced phase transition in relaxor ferroelectric crystals". In this work, a thermodynamics based analysis of measured material behavior in <110> orientated

(PMN-32%PT) and (PZN-4.5%PT) crystals under combined stress, electric field and temperature loading leads to a determination of the relative energy levels of phases. The approach is to perform path integrals to determine external work done by electrical and mechanical loads at constant temperature and to remove the effect of heat generated by irreversible strain and electric displacement increments. This yields relative internal energy density levels of phases. It also yields Gibbs energy density, a measure of the driving force for the phase transformation. The technique is demonstrated for two types of phase transition, a jump type transition from rhombohedral to orthorhombic with associated hysteresis in [011] loaded PZN-4.5%PT, and a continuous transition from rhombohedral to orthorhombic with rotation through an intermediate monoclinic phase in [001] loaded PMN-32%PT.

Liu and Lynch [31] published a paper in Integrated Ferroelectrics entitled "Characterization and modeling of relaxor single crystals". This work describes the application of micromechanical approached to understanding the domain switching and phase transformation behavior of relaxor single crystals.

Oates and Lynch [32] participated in a collaboration with TU-Darmstadt in which they modeled the fracture behavior of ferroelectric ceramic specimens with edge notches subjected to electric field.

Webber, Zhu, and Lynch have submitted an article for publication in Acta Materialia entitled "Ceramic and Single Crystal (1-x)PMN-*x*PT Constitutive Behavior under Combined Stress and Electric Field Loading" in which the electromechanical behavior of single crystals and ceramics of the same composition are compared under combined stress and electric field loading.

In addition to the refereed journal articles, Liu and Lynch have contributed two book chapters that review the behavior of ferroelectric single crystals.

Liu, T., C.S. Lynch, Book Chapter "Advances in Adaptive Materials and Adaptive Structures", AIAA Progress in Astronautics and Aeronautics, Edited by Norman Wereley, George Lesierte, and Dimitris Lagoudas (2006)

Liu, T., C.S. Lynch, Advanced Dielctric, Piezoelectric, and Ferroelectric Materials – Synthesis, Characterization and Applications, Chapter 14 (2007)

Kyle Webber is currently working on his PhD performing modeling of field induced phase transformations in relaxor single crystals. He has completed his qualifying examinations and coursework, and should complete his PhD in approximately 6 months. His recent efforts have been directed at modeling the constitutive behavior of relaxor single crystals. To date, domain engineering has largely meant identifying the physical properties of the [111] single domain crystal and performing orthogonal transformations to find the properties of other crystal cuts. Although this works well for certain stable domain states such as [001] and [011], in most cases application of electric field or stress preload will induce sufficient domain wall motion to significantly change the properties of the crystal (repolarization). Webber's modeling is incorporating the effects of field induced repolarization and phase transformation into the domain engineering models.

References:

[1] McLaughlin EA, Liu T, Lynch CS. Acta Mater 2004; 52(13):3849.

[2] Viehland D, Amin A, Li JF. Appl Phys Lett 2001; 79(7):1006.

[3] Zhao X, Fang B, Cao H, Guo Y, Luo H. Mater Sci Eng B 2002; 96(3):254.

[4] Nye JF. Physical properties of crystals: their representation by tensors and matrices. London: Oxford University Press, Oxford, 1967.

[5] Xu G, Luo H, Xu H, Yin Z. Phys Rev B 2001; 64(2):020102.

[6] Noheda B, Cox DE, Shirane G, Gao J, Ye G. Phys Rev B 2002; 66(5e):054104.

[7] Ye Z-G. Curr Opin Solid State Mater Sci 2002; 6(1):35.

[8] Singh AK, Pandey D. Phys Rev B 2003; 67(6):064102.

[9] Uesu Y, Yamada Y, Fujishiro K, Tazawa H, Enokido S, Kiat JM, Dkhil B. Ferroelectrics 1998; 217(1):319.

[10] Fujishiro K, Vlokh R, Uesu Y, Yamada Y, Kiat M, Dkhil B, Yamashita Y. Jpn J Appl Phys , Part 1 1998; 37:5246.

[11] Belegundu U, Du XH, Cross LE, Uchino K. Ferroelectrics 1999; 221(1-4):67.

[12] Ye Z-G, Dong M, Zhang L. Ferroelectrics 1999; 229:223.

[13] Ye Z-G, Dong M. J Appl Phys 2000; 87(5):2312.

[14] Bertram R, Reck G, Uecker R. J Cryst Growth 2003; 253(1-4):212.

[15] Liu SF, Park SE, Shrout TR, Cross LE. J Appl Phys 1999; 85(5):2810.

[16] Ren W, Liu SF, Mukherjee BK. Appl Phys Lett 2002; 80(17):3174.

[17] Noheda B, Cox DE, Shirane G, Guo R, Jones B, Cross LE. Phys Rev B 2001; 63(014103):1.

[18] Viehland D. J Appl Phys 2000; 88(8):4794.

[19] Park SEE, Hackenberger W. Curr Opin Solid State Mater Sci 2002; 6(1):11.

[20] Chen K-P, Zhang X-W, Luo H-S. J Phys : Condens Matter 2002; 14:571.

[21] Han J, Cao W. Phys Rev B 2003; 68(13):134102.

[22] Schmidt VH, Chien R, Shih IC, Tu C-S. AIP Conf Proc 2003; 677(1):160.

[23] Tu C-S, Huang LW, Chien R, Schmidt VH. AIP Conf Proc 2003; 677(1):152.

[24] Tu C-S, Shih IC, Schmidt VH, Chien R. Appl Phys Lett 2003; 83(9):1833.

[25] McLaughlin, Elizabeth A.; Liu, Tieqi; Lynch, Christopher S; Relaxor ferroelectric PMN-32%PT crystals under stress, electric field and temperature loading: II-33-mode measurements Acta Materialia, v 53, n 14, August, 2005, p 4001-4008

[26] Liu, T.; Lynch, C.S. Characterization and modeling of relaxor single crystals *Integrated Ferroelectrics*, v 71, 2005, p 173-9 (2005)

[27] Lynch with T. Liu, "Orientation Dependence of Non-linearity and Hysteresis in PZN-4.5%PT Single Crystals I – Unipolar Response" Accepted JIMSS 05

[28] Lynch with T. Liu, "Orientation Dependence of Non-linearity and Hysteresis in PZN-4.5%PT Single Crystals II –Bipolar Response" Accepted JIMSS 05

[29] Liu, T. Lynch, C.S. "Domain engineered relaxor ferroelectric single crystals" *Continuum Mechanics and Thermodynamics*, v 18, n 1-2, August, 2006, p 119-135

[30] Liu, McLaughlin, and Lynch, Thermodynamics of Phase Transformations in Ferroelectric Single Crystals, Accepted *JIMSS*, February, 2006

[31] Liu, T.; Lynch, C.S. "Characterization and modeling of relaxor single crystals" *Integrated Ferroelectrics*, v 71, 2005, p 173-9

[32] Westram, Ilona; Oates, William S.; Lupascu, Doru C.; Rodel, Jurgen; Lynch, Christopher S. "Mechanism of electric fatigue crack growth in lead zirconate titanate" *Acta Materialia*, v 55, n 1, January, 2007, p 301-312

[33] Webber, Zhu, Lynch, "Ceramic and Single Crystal (1-x)PMN-*x*PT Constitutive Behavior under Combined Stress and Electric Field Loading" submitted to Acta Materialia July, 2007